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Water quality in Malawi
– Effluent water from a matchstick factory in Blantyre

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Cover: Matchstick box from the Leopard factory in Blantyre, 2013, photo by author

Abstract

Fresh drinking water and basic sanitation is one of the Millennium Development Goals adopted by the United Nations. Poorly cleaned water may expose living organisms to diseases such as cholera and diarrhea to mention a few. This study was executed in Blantyre, the second largest city in Malawi. Blantyre is a commercial centre with many industries and the city's population has grown quickly during the past years. Even though the popula- tion has grown and the number of heavy industries has increased making the demands for clean freshwater, waste disposal and functioning water sanitation more urgent than ever.

In this study effluent water from a matchstick factory in Blantyre has been investigated. The method of grab sampling was performed in May 2012 and the metal ions analyzed were chromium, zinc and potassium, as all of them are used in the production. The inor- ganic anions sulfate, nitrate and chloride were also analyzed. The results were compared to the limit values for effluent water according to the Malawian Bureau of Standards. The concentration of chromium, zinc and nitrate ions were above the tolerance limit. The efflu- ent from the factory goes directly to the Blantyre Wastewater Treatment Plant and for fu- ture studies it is suggested that water samples taken after the treatment plant are analyzed to investigate if the ion concentrations are still too high.

Keywords: matchstick, chromium, zinc, potassium, inorganic anions, industrial wastewater treatment

Abbreviations

AAS	Atomic Absorption Spectrophotometry
APHA	American Public Health Association
IC	Ion exchange chromatography
MBS	Malawian Bureau of Standards
WHO	World Health Organization

Table of contents

1 Introduction

1.1 Overview and background

Access to fresh water is of utmost importance for all living organisms. The human body contains about 60 % of water and every human daily needs several litres of fresh drinking water (Baird and Cann, 2008). Daily chores such as showering, washing and cooking also require fresh water. More than 97 % of the total water basin of the world is seawater. Rivers and lakes mare the main source for fresh water and they make up only 0.01 % of the fresh water basin (Baird and Cann, 2008).

One of the goals in the Millennium Development Goals adopted by the United Nations in 2000 is to "*by 2015 halve the proportion of the population without sustainable access to safe drinking water and basic sanitation*" (MDG, 2000). In the report *Guidelines for drinking-water quality* by the World Health Organization, even though improvements have been done, it is estimated that 780 million people do not have access to fresh drinking water (WHO and UNICEF, 2012). In the developing countries there is still lack of sanitary equipment to clean the water. In- sufficient water treatment can result in diseases like cholera, diarrhea, and bilhazias among others (Kuyeli et al., 2009).

Recent studies (Sajidu et al, 2007) have shown high levels of some heavy metals in the rivers of Blantyre, Malawi. Blantyre is the second largest city in Malawi with a population of 694 500 (Nationalencyklopedin, 2012a). The city is the main commercial centre in Malawi with many industries (Nationalencyklopedin, 2012a). There are numerous waterways running through the city, including Mudi, Nasolo and Limbe Streams. Over the past years the population in Blantyre has

grown fast, increasing the demands for clean fresh water, safe waste disposal and functioning water sanitation (Sajidu et al., 2007). Heavy metals occur in soils naturally that can leach into water streams. They can also reach water bodies through unauthorized deposition of incompletely treated industrial effluents. The determination of harmful substances from industries in Blantyre is important to protect public health, the environment and the food safety.

This study investigated the chemical composition of effluent from the Leopard Matchstick factory in Blantyre to determine the substances entering the municipal sewage system line to the Blantyre Wastewater Treatment Plant. The chemicals identified in the production process are given in table 1.

Table 1. *Chemicals identified in the production*

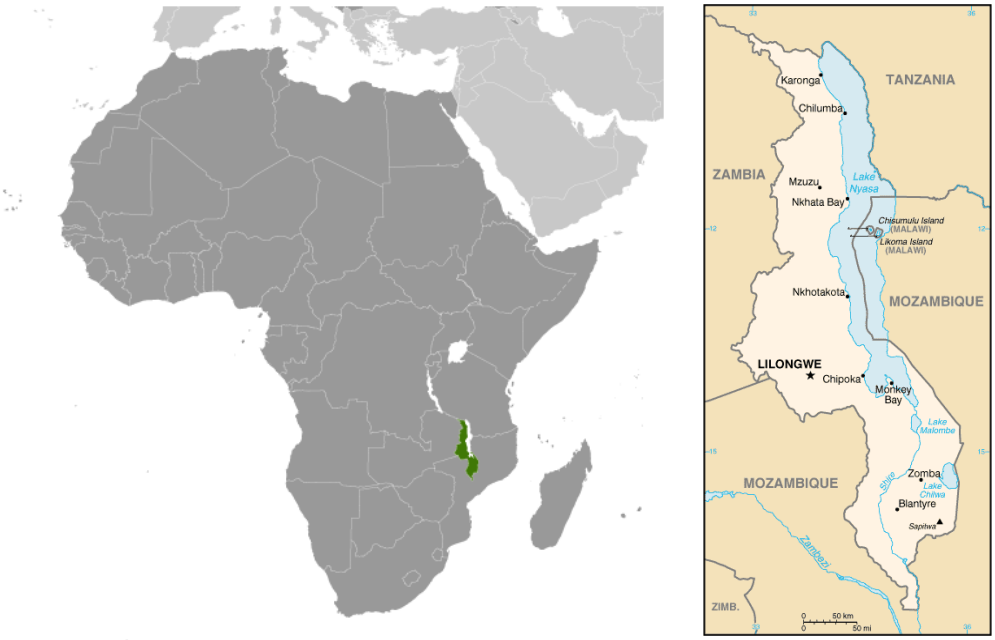
Chemicals used in the production
Dry chemicals mix
Sulfur
Glass flour
Limestone, $CaCO_3$
Kaolin, $Al_2Si_2O_5(OH)_4$
Zinc oxide, ZnO
Talc, $Mg_3Si_4O_{10}(OH)_2$
Hide glue mix
Hide glue
Gelatine
Red pigment
Water
Starch mixture
Potassium dichromate, $K_2Cr_2O_7$
Starch
Water
Formaldehyde 3 %, HCHO

1.2 Description of the study site

1.2.1 Malawi

Malawi is situated in the south-central Africa and is bordered by Tanzania, Zambia and Mozambique, se Figure 1. The capital city is Lilongwe with a population of 723 600. The country covers an area of 118 484 km^2 with a total population of 15.3 million, and is one of the most densely populated countries in Africa with an estimated population density of 135 citizens per km^2 (Briggs, 2010). More than 50 % of the population lives in the southern region, compared to the 12 % in the northern part. Malawi lies along the East African rift valley, with high mountain massifs and plateaus; examples are the Nyika plateau measuring 2 606 m.a.s.l. and the Mulanje Massif where Sapitwa is the highest peak with 3 002 m.a.s.l. The most famous feature in the landscape, Lake Malawi, is the third largest lake in Africa, 570 km long, and accommodates among other wildlife approximately 500 species of endemic cichlids. The only outlet from the lake is the Shire River, which is supporting the Shire Valley with water, before it connects with the Zambezi River in Mozambique (Nationalencyklopedin, 2012b).

The most important economic sector is the agriculture, engaging 85 % of the working population. In 2011 the BNP per capita was 350 US dollars where the agriculture is responsible for 33 %. The most important food crop is maize which is cultivated by most farmers. From the maize *nsima* is made, the staple food in Malawi. Other important crops are cassava, sorghum, peanuts, rice, leguminous plants, tea and tobacco (Nationalencyklopedin, 2012b).



10 **Figure 1. Malawi is shown in green together with the surrounding countries. From The World Factbook (2012)**

1.2.2 Blantyre

Blantyre is situated in the southern region of the country in the lower Shire Valley. It was founded in 1876 and named after British explorer David Livingstones birth place in Scotland. The effluent collected for this study is from the Leopard Match Factory situated in the central part of Blantyre (Nationalencyklopedin, 2012a). Wastewater from the factory is stored in a pond, letting bigger particles settle before the water is led to the Blantyre Wastewater Treatment Plant.

1.3 Objective

The main objective of this study was to determine the chemical characteristics of effluent from the matchstick production factory. The specific objectives were to

i) Determine the concentration of total chromium, potassium and zinc with atomic absorption spectrophotometer, AAS

ii) Determine the concentration of sulfate, nitrate and chloride with ion chromatography, IC

1.3.1 Limitations

Due to a limited amount of time and necessary equipment, only total chromium concentration was analysed and no separation between trivalent and hexavalent chromium was possible.

2 Literature review

2.1 Heavy metals

There is a wide range of meanings to the term heavy metal, there is however no general agreement of the term. It is often used to name a group of metals associated with toxicity and contamination (Duffus, 2002). Many of the heavy metals are essential in small amounts for plants and animals, but highly toxic in larger quantities and concentrations (HSR, 2012). They have the ability to bio- accumulate; the concentration increases over time in a biological organism, compared to the concentration in the environment (Lenntech, 2012).

2.1.1 Chromium

Chromium is a transition metal with the molar mass of 51.9 g/mol (Nationalencyklopedin, 2012d). The French chemist Louis Vauquelin discovered the metal in 1797 and was given the name chromium from the Greek word *chroma* meaning colour (Mohan and Pittman Jr., 2006). It is the twenty-first most abundant element in the earth's crust, about 120 g/ton (Mohan and Pittman Jr. and Nationalencyklopedin, 2012d). Chromium can occur in several oxidation states like +II, +III and +VI although the +II state is very unstable in presence of traces of oxygen (Mohan and Pittman Jr., 2006). Trivalent chromium hydrolyses easily to soluble $CrOH^{2+}$, $Cr(OH)_2^-$, $Cr(OH)_4^-$, complexes starting at pH≈3 at higher chromium(III) concentrations and polynuclear complexes as $Cr_2(OH)_2^{4+}$, $Cr_3(OH)_4^{5+}$ and $Cr_4(OH)_6^{6+}$. Chromium(III) precipitates as solid chromium(III)oxide, Cr_2O_3, in the pH range 5-12. Chromium(III)oxide has low solubility which leads to that the chromium(III) concentrations in neutral water is low (Baes Jr. and Mesmer, 1976). Hexavalent chromium is only present as neutral and anionic

species, where chromate CrO_4^{2-}, hydrogen chromate, $HCrO_4^{2-}$ and dichromate, $Cr_2O_7^{2-}$, are the most common ones. Chromic acid, H_2CrO_4,dominates when the pH is less than 1.0 and the hydrogen chromate ion, $HCrO_4^-$, is dominant in pH range of 1.0 and 6.0. The chromate ion, CrO_4^{2-}, predominates at pH above 6.0 (Mohan and Pittman Jr., 2006). Figure 2 shows a redox potential Eh-pH diagram where the different oxidations states and chemical forms are presented within a diluted Eh and pH ranges.

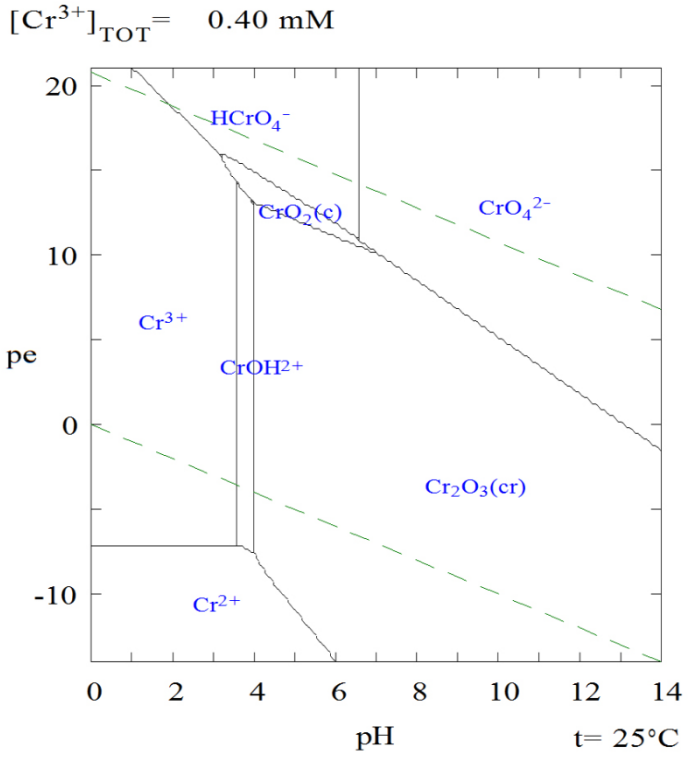


Figure 2. Predominance diagram for chromium. $(Cr^{3+})_{tot}$=0.40 mM at 25°C. From Puigdomenech, I. (2011).

For trivalent chromium, the hydrated ion, $Cr(H_2O)_6^{3+}$ dominates at pH ≤ 3, and at pH 3, hydrolysis occurs to form trivalent chromium hydroxyl species as $CrOH^{2+}$, $Cr(OH)^{2+}$, $Cr(OH)_3(s)$ and $Cr(OH)_4^-$, $Cr_2(OH)_2^{5+}$ and $Cr_4(OH)_6^{6+}$ depending on the level of pH and total chromium(III) concentration.

High water solubility and mobility and high toxicity make chromium(VI) compounds much more problematic than chromium(III) ones (Mohan and Pittman Jr., 2006). Because of the strong oxidizing characteristics of chromium(VI), it is harmful to biological systems. Exposure of the hexavalent chromium causes skin irritation, kidney and liver damages, and respiratory problems and increases the risk of cancer (Chromium health surveillance guidelines, 2010). The Malawi Bureau of Standards, MBS, tolerance limit for total chromium in effluent water is 0.05 mg/L (MS 539: 2002).

Chromium is mainly used as an alloy metal to increase the hardness, mechanical strength and resistance against corrosion and oxidation. The metal is also used in the production of chemical compounds used for chrome plating, textile dying, wood impregnation and production of colour pigment and catalysts (Nationalencyklopedin, 2012d). Because of the different oxidation states and the ability to form compounds with other elements, chromium compounds show a range of various colours. Chromium(III) oxide has a green colour, chromium(VI) oxide appears dark red, the dichromate, $Cr_2O_7^{2-}$, is orange-red and the chromate ion, CrO_4^{2-}, yellow. Gemstones such as emeralds and rubies are given its colour because chromium(III) has replaced a small amount of the aluminum(III) ions in the minerals (Nationalencyklopedin, 2012d).

2.1.2 Potassium

Potassium has the molar mass of 39.10 g/mol and occurs generally as silicate minerals such as orthoclase (Chang, 2007). Potassium is the seventh most abundant element in the earth's crust and hydrosphere (Nationalencyklopedin, 2012e). In 1807 Sir Humphry Davy managed to separate metallic potassium and sodium, but before that different chemical compounds containing sodium and potassium ions were used as detergents (Nationalencyklopedin, 2012e).

Potassium is a soft, silver coloured metal with a high electric conductivity. Its electron configuration is $[Ar]4s^1$, where the only valence electron makes the metallic bonding weak. The low electron negativity makes potassium highly reactive. It

is often used as a reducting agent and can react with most metals and non-metals (Nationalencyklopedin, 2012e). Potassium is present in all plant and animal tissues as an essential element. It maintains the normal osmotic pressure in cells and operates with many enzymes in the metabolism (WHO, 2009). Potassium is always found as the potassium ion, K^+, and forms compounds with many elements. Potassium oxides forms when potassium and oxygen reacts and can form K_2O, K_2O_2 and KO_2. Superoxide, KO_2 is used as an air purifier and is common in submarines. Potassium hydroxide, KOH, is used to produce soap (Nationalencyklopedin, 2012e).

2.1.3 Zinc

Zinc belongs to the post-transition metals and has the molar mass 65.39 g/mol (Nationalencyklopedin, 2012f). It is the twenty-fourth most abundant element in the Earth's crust with about 775 ppm (Chang, 2007). Zinc occurs mostly in chemical compounds and rarely as metallic zinc. The most common zinc mineral is sphalerite, ZnS, which is also called zincblende (Nationalencyklopedin, 2012f). In addition to metallic zinc the only oxidation state is Zn^{2+}. In weak acidic media Zn^{2+} hydrolyses to form $ZnOH^+$ and Zn_2OH^{3+} and in alkaline media to $Zn(OH)_4^{2-}$ and $Zn_2(OH)_6^{2-}$ (Baes Jr. and Mesmer). In Figure 3 a Pourbaix diagram is presented for zinc at 25° and with the concentration of 10^{-4} molal, which is a more diluted system than the effluent water studied.

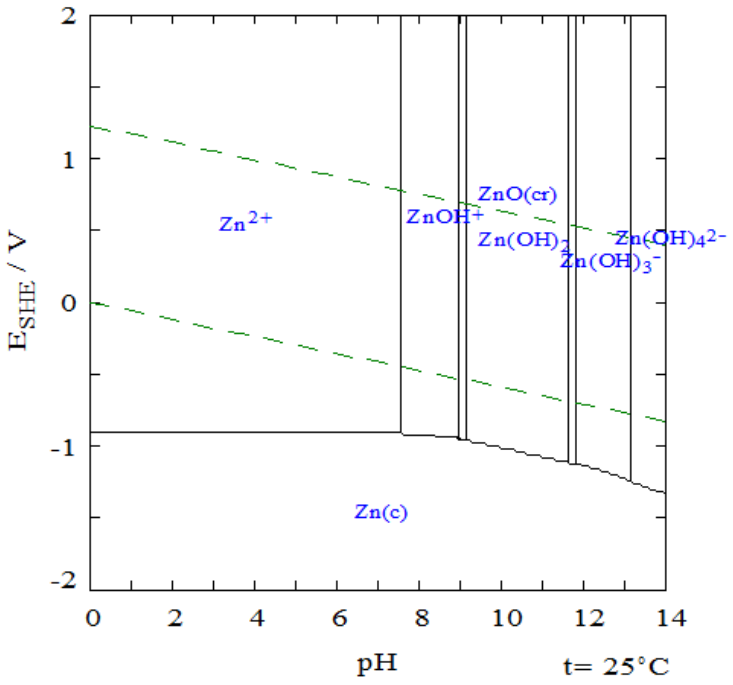


Figure 3. Pourbaix diagram for zinc at 25° C and $[Zn^{2+}(aq)]_{tot}$=10 µM. From Puigdomenech, I. (2011)

Zinc is an essential element, important for microorganisms, plants and animals. Zinc(II) is found in many proteins as an important component in enzymes for metabolism and regulation in the activity of genes (Nationalencyklopedin, 2012f). The main use of metallic zinc is as surface finishing and as corrosion resistance for iron and steel. Zinc is also used for alloys and as ingredients for production of catalysts, batteries, pigments, impregnation and antisepsis compounds among others. The tolerance limit for zinc in industrial effluents is 5 mg/l according to the MBS (MS 539:2002).

2.2 Inorganic anions

2.2.1 Sulfate

The sulfate anion, SO_4^{2-} is very stable in water. Naturally sulfates occur in minerals such as barite, $BaSO_4$, epsomite, $MgSO_4 \cdot 7H_2O$. In natural waters dissolved sulfate contributes largely to the sulfur content (WHO, 2004). The tolerance limit for sulfate according to the Malawian Bureau of Standards for wastewater is 800 mg/l (MS 539:2002).

2.2.2 Nitrate

Nitrates are salts or esters formed from nitric acid, HNO_3. Nitrates are common salts with great importance for production of fertilizers and explosives. Access of nutrients like nitrate in water systems contributes to eutrophication (Nationalencyklopedin, 2012g). According to the Malawian Bureau of Standards the tolerance limit for nitrate in wastewater is 50 mg/l (MS 539:2002).

2.2.3 Chloride

The chloride ion is formed when chlorine gains an extra electron. The anion is present in low amounts in most natural waters and most of its salts are very soluble. The hydrated chloride ion is normally not involved in oxidation and reduction reactions, but forms complexes with a wide range of metal ions (Nationalencyklopedin, 2012h).

2.3 Safety matches

A safety match is a small piece of wood with a solidified mixture of chemicals. When the head of the stick is struck on a special surface the friction causes the stick to ignite. According to the Leopard Match factory in Blantyre 40 000 boxes of matches are produced every day (Personal communication, 2012-05-02).

2.3.1 What ignites the matches?

When the matches are stroken against the striking surface of the box, heat emerges due to friction. Small amounts of red phosphorous are transferred from strike surface to the head and with the oxygen from the air as a catalyst, a reaction between potassium chlorate and phosphorous ignite the matches (Nationalencyklopedin, 2012j).

2.3.2 History

The first known matches can be dated back to 577 AD in China. Sticks coated in chemicals were used by the women in the villages to start fires for cooking (Cavette, 2008). Under the Roman Empire matches made from pine dipped in sulfur was common because of their ability to easily ignite. The first match made by phosphorous was invented in 1827 by the English chemist John Walker. The strike surface was made by white phosphorous that could be ignited by friction. The toxicity of the yellow and white phosphorous made the matches hazardous to both the workers and users of the matches (Tändsticksmuséet, 2012).

In 1841, the Swedish chemist and inventor Gustaf Erik Pasch became a company member of the first matchstick factory in Sweden. He removed the white phosphorous and introduced a separate striking surface with red phosphorous as the active ingredient. The matches became too expensive and the fabric closed down in 1848. Johan Edward and Carl Frans Lundström did experiments with the safety match and built a factory for production. When the patent from Pasch ceased to exist the brothers could obtain a patent for their new and improved safety match. In 1868 the price of the red phosphorous had been reduced and the production became mechanized and the match became more popular on the market (Tändsticksmuséet, 2012).

2.3.3 Production

The production of safety matches in the Leopard Match Factory proceeds in the same way safety matches have been produced since the 19th century. Veneer arrives to the factory, where it is chopped into splint and transported into slowly rotating cylinders. First, the splint goes through impregnation with ammonium dihydrogenphosphate, $(NH_4)H_2PO_4$, to prevent the matches from smoldering after they have gone out. The splints are then placed in a large rotating drum to dry. The dried and polished splints are then transferred to a machine that separates the flawless splints from the defective ones. From the storage area, the splints are transferred via a conveyor belt into a perforated steel belt. The sticks are dipped into hot paraffin wax, to help the flame to transfer from the chemicals on the tip to the stick itself. When the matchsticks are dry once again, they are dipped in a solution to form the head of the sticks (Guided tour at the Leopard Matchstick factory, 2012-05-02). Typically, the solution used for the match head is a mixture of chemicals. Potassium chlorate, $KClO_3$, works as a fire retardant when reacting with red phosphorous. Sulfur and starch are added to give the solution the right texture together with a neutralizer, zinc oxide or calcium carbonate. Siliceous filler is added as well to work adhesive. The striking surface on the matchboxes is usually composed of powdered glass and red phosphorous, with carbon black as additional pigment, neutralizer and binding material (Calvert, J.B, 2002). Potassium dichromate, $K_2Cr_2O_7$, is used as a catalyst in the matchstick headto lower the activation energy in the ignition reaction (Jonas Nordqvist, Swedish Match, 2012-04-17). Finally the ready matches are being filled into the boxes and packaged (Guided tour at the Leopard Matchstick factory, 2012-05-02).

Figure 4. The veneer is chopped into splints.

Figure 5. The ready matchsticks are being sorted into the boxes.

2.4 Brief introduction to Atomic Absorption Spectrophotometry and Ion exchange Chromatography

In this study, atomic absorption spectrophotometry and ion chromatography are the primary analytical methods used. The following parts briefly explain the function of the methods.

2.4.1 Metal ion detection with Atomic Absorption Spectrophotometry

Atomic absorption spectrophotometry is an analysis method to quantitatively determine dissolved element at medium to low concentrations. The sample is sprayed into a flame, the most common one being an acetylene and air. Elements transmit radiation at specific wavelengths and to measure the amount of the element in the solution, the radiation absorbed from a lamp is measured. The absorption increases with increasing concentration of the element in the sample according to the Beer-Lambert- law $A = \varepsilon \times l \times c$. The result from the absorption is then compared with the result from calibration measurements using standard solutions (Skoog et al, 2004). The method of standard addition is frequently used in atomic absorption spectrophotometry. Different known volumes of a solution are added to the sample and a linear regression curve is fitted to the calibration. This method is useful to detect if the sample is affected by other factors i.e. temperature (Harris, 2003).

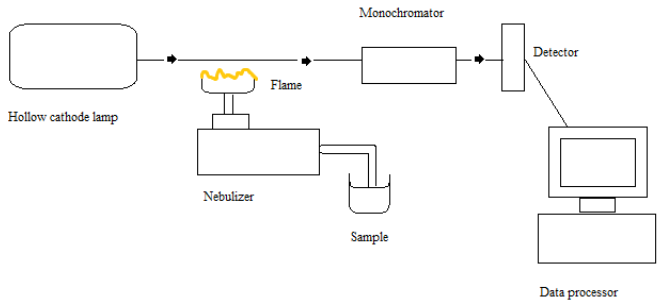


Figure 6. Schematic picture of the AAS process. After Skoog et al, 2004.

2.4.2 Ion exchange chromatography

An ion exchange chromatography is used to measure the amount of anions. The ions in the sample are transported with an elution fluid in a column where the separation is takes place. The stationary phase in the in the column has charged functional groups and they are responsible for the ion exchange. Depending on the pH, temperature, flow rate, the ion strength and composition of the elution fluid, the ions transported at different rates through the separation column. A detector measures the retention time and the amount of the ions, and the result is compared to standard solutions (Skoog et al, 2004).

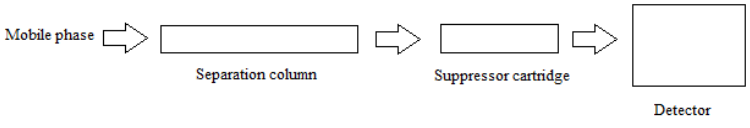


Figure 7. Schematic picture of the IC process. After Skoog et al, 2004.

3 Materials and methods

3.1 Materials

The study site for the project was the Leopard Match Factory in Blantyre, southern Malawi. Wastewater samples were collected in May 2012 at the discharge point of the factory, Figure 8.

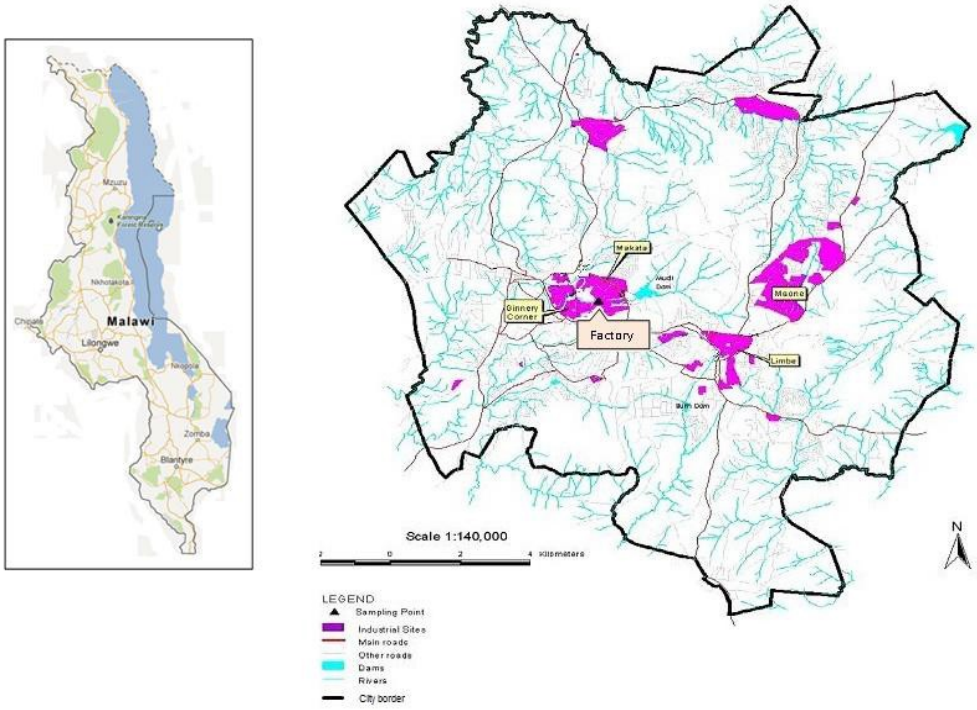


Figure 8. Map over Blantyre city with industrial sites marked in purple. The sampling point marked as factory. After Sajidu et al, 2007.

3.2 Methods

3.2.1 Sample collection

Sampling was performed using the method of so-called grab sampling according to APHA (1976). Two 1l plastic containers were collected with wastewater. Conductivity and pH (Oakton Instruments, EcoTestr. Model pH2) were measured and 1.5 ml of nitric acid was added to one of the bottles to minimize precipitation and adsorption on the walls of the bottle. The container without acid was sealed and stored in refrigerator.

Figure 9. Sampling collection at the discharge point at the factory, 2012-05-02

3.2.2 Preparation of samples

The samples were treated in different ways depending on the analytical methods used. Atomic absorption spectrophotometry was used to determine the concentrations of the metal ions and ion chromatography for the anions.

3.2.3 Determination of metal ions

Digested samples

The samples for AAS measurements were prepared following the method from APHA. 100 ml of the acidified samples was transferred to a 250 ml beaker, where 5 ml concentrated nitric acid was added and the mixture was placed on a hot plate letting it heat to a simmering. When approximately 20 ml remained of the mixture, an additional 5 ml of 10 % nitric acid was added and the beaker was covered with a watch glass. Another 5 ml nitric acid was added and the mixture was left to boil until a clear, light coloured solution was obtained. The solution was filtered and diluted to 100 ml (APHA, 1976).

Undigested samples

150 ml of the sample were filtered through an 11 µm Whatman filter paper, 50 ml each into three 100 ml plastic flasks.

For the determination of chromium where organic substances in the sample could cause interference through absorption at the same wavelength on additional step was added. 1 g of activated charcoal was added to 100 ml of the water sample to absorb the organic substances. It was left to shake for 1 hour in a shaker (Stuart Mini Orbital Shaker, SSM1) and subsequently filtered through a vacuum filter.

Analysis of the digested and undigested sample

The concentrations of chromium, potassium and zinc were determined using atomic adsorption spectrophotometry (Buck Scientific Model 200A) at Chancellor College, University of Malawi.

3.2.4 Determination of inorganic anions

Sample treatment

100 ml of the refrigerated sample was filtered through a Whatman 11 µm filter paper. 5 ml of the filtrate was diluted to 50 ml. An additional 12 ml of the sample was filtrated through a Cronus pes 0.45 µm into three 100 ml plastic bottles, with 4 ml in each.

Analysis of the sample

A component suppression ion chromatography system composed of a Dionex CDM-1 conductivity detector, an Ionpac AS14 anion exchange column and Data Apex Clarity chromatography software, was used to determine the sulfate, nitrate and chloride ion concentration at Chancellor College.

4 Results and discussion

This section presents the results from the atomic absorption spectroscopic measurements and the ion chromatographic measurements for the digested and undigested samples. At the time of the sampling the pH value observed was 6.5 and the conductivity 2900 µS.

4.1 Determination of metal ions

The concentration of the metal ions in the water effluent is given in Table 2. The concentrations for the digested and undigested sample for total chromium, potassium and zinc as well as the limit values according to the Malawian Bureau of Standards are given (MS 539:2002) are given as well.

Table 2.*Concentration of total chromium, potassium and zinc in the samples*

Concentration/ mg·l^{-1}]			
	total chromium, Cr_{tot}	potassium, K^+	zinc, Zn^{2+}
Digested sample	13.5	438	7.10
Undigested sample	33.3	3693	3450
Limit value MBS	0.05	n/a	5

The concentration for chromium in both samples were much higher than the tolerance limit from the MBS, 0.05 mg/l. There is quite a difference between the digested and the undigested sample. The digestion is made to remove color and organic material before the sample is analyzed in the AAS to avoid interferences. Activated charcoal was added to the undigested sample and then filtered through a vacuum filter pump. The digestion is a more powerful method that should release

all possible complexes and convert the metals into soluble forms. A possible explanation to why the undigested sample has a higher concentration of the total chromium is that there are still some organic substances that absorbs at the same wavelengths as the chromium. In the factory, there are a lot of substances and chemicals used in the production and it is possible that some pigment in the solution was still present in the solution when analyzed in the atomic absorption spectroscopy. To prevent this kind of possible interferences, the solution should be run at least at one more wavelength where chromium absorbs. A blank sample with the activated carbon was run in the AAS to make sure that there were no impurities in the carbon itself. It is also possible that some of the chromium were absorbed by the carbon, although this does not explain the higher values with the undigested method.

The pH in the effluent was at the time of sampling 6.5. According to Figure 2, at the current concentration measured in the effluent, it is likely that there is a mixture of hydrogen chromate and chromate ions (Mohan and Pittman Jr., 2006). In water with a high DOC content, the chromium(III) ions could be in complexes with the DOC or in the suspension. The chromium is thus not oxidized to chromium(VI) but remains in the trivalent state (Essington, 2004). When the nitric acid was added to the containers with the sample water the pH decreased to below 2. At low pH values it is likely that there is a mixture of various chromium species, mainly chromate acid and hydrogen chromate ions (Mohan and Pittman Jr., 2006).

Because of limited time and the necessary equipment for a separation between trivalent and hexavalent chromium, only the total chromium was determined. Although, the red color of the effluent is suggesting that hexavalent chromium is the dominating form. There are methods available to separate chromium(III) and chromium(VI). Diphenylcarbazide can be used in the colorimetric method to form complexes with Cr(VI), or an alkaline digestion of the sample can be made to measure the concentration of chromium(VI) (Parks et al., 2004).

The zinc concentrations measured were 7.1 mg/l in the digested sample and 3450 mg/l in the undigested sample. Also here, the concentration should be higher in the digested sample since the digestion destroys the different zinc containing compounds and releasing zinc ions in the solution. Particles containing of larger zinc compounds could have been separated from the solution in the undigested sample, when the solution was filtered. At pH 6.5, zinc exists in the hydrated form in the

effluent water, as shown in Figure 3.

Potassium concentrations were 483 mg/l in the digested sample and 3693 mg/l in the undigested sample. Alkali metal ions such as potassium ions are very soluble in water, so there should not really be any difference between the digested and undigested samples.

When the samples were collected the production was not up, suggesting that the concentrations of the metals are higher when the factory is running. The method of standard addition could have been tried in order to control the results from the AAS.

4.2 Determination of inorganic anions

Table 3 summarizes the concentration of the anions determined by ion chromatography. The results for chloride, nitrate and sulfate is shown together with the tolerance limit for wastewaters as stated by the MBS (MS 539:2002).

Table 3. *Concentration of chloride, nitrate and sulfate in the sample*

Concentration/ mg $\cdot l^{-1}$			
	Chloride	Nitrate	Sulfate
Sample	12±6.2	536±260	3.5±4.5
Limit value MBS	n/a	50	800

The effluent showed relatively low levels of chloride, but there is no tolerance limit set for chloride by the MBS.

The concentration of nitrate in the effluent water was 536 mg/l, which is significantly higher the tolerance limit from the MBS, 50 mg/l. It is difficult to know the possible source for the nitrate, but since the water entering the factory was not measured, it could already contain increased nitrate levels. When the effluent water reaches the water treatment it will be diluted in the water, but such high levels can cause eutrophication in the rivers in Blantyre. The hexavalent chromium is a strong oxidizing agent, could potentially oxidize ammonium, NH_4^+ to nitrate, NO_3^- in the effluent.

The sulfate level in the effluent was much lower than the tolerance limit. The origins for the sulfate could be the sulfur used in the mixture for the matchstick head.

4.3 Sources of error

There are several circumstances that could affect the results presented in this study. The main problem was the old and poor equipment resulting in difficulties readings and lack of sufficient distilled water. The samples were replicated numerous of times to check the credibility in the results. These replications have shown a wide variation, making it difficult to interpret the result most likely to be the most correct one. During the time of sampling it was not possible to measure the water entering the factory, thus a comparison between the effluents was not possible. This would have been necessary to surely determine the affect the match production have on the water.

5 Conclusions and recommendations

The concentrations of total chromium, zinc and potassium were measured with AAS, and concentrations of chloride, sulfate and nitrate were measured with IC. The conclusions that can be drawn from this work are that the concentration of metals such as chromium and zinc is largely exceeding the tolerance limit set by the Malawian Bureau of Standards for wastewater. High levels of chromium and especially high levels of the hexavalent species are very toxic. In this study it was not possible to separate tri- and hexavalent chromium, but there are methods available making it possible. The levels of nitrate were also much higher than the tolerance limit. The wastewater from the factory leads directly to the wastewater treatment plant, and will therefore be diluted in the water masses before it enters the river system in and around the city of Blantyre. For improving the water quality in Blantyre, further studies should be made to determine the concentrations of the metals and anions in the wastewater from the factory more accurately. Sampling should also be performed on the treated water after the water treatment plant, to detect if the concentrations are still high after the dilution and the water treatment using the new instruments now available at Chancellor Collage.

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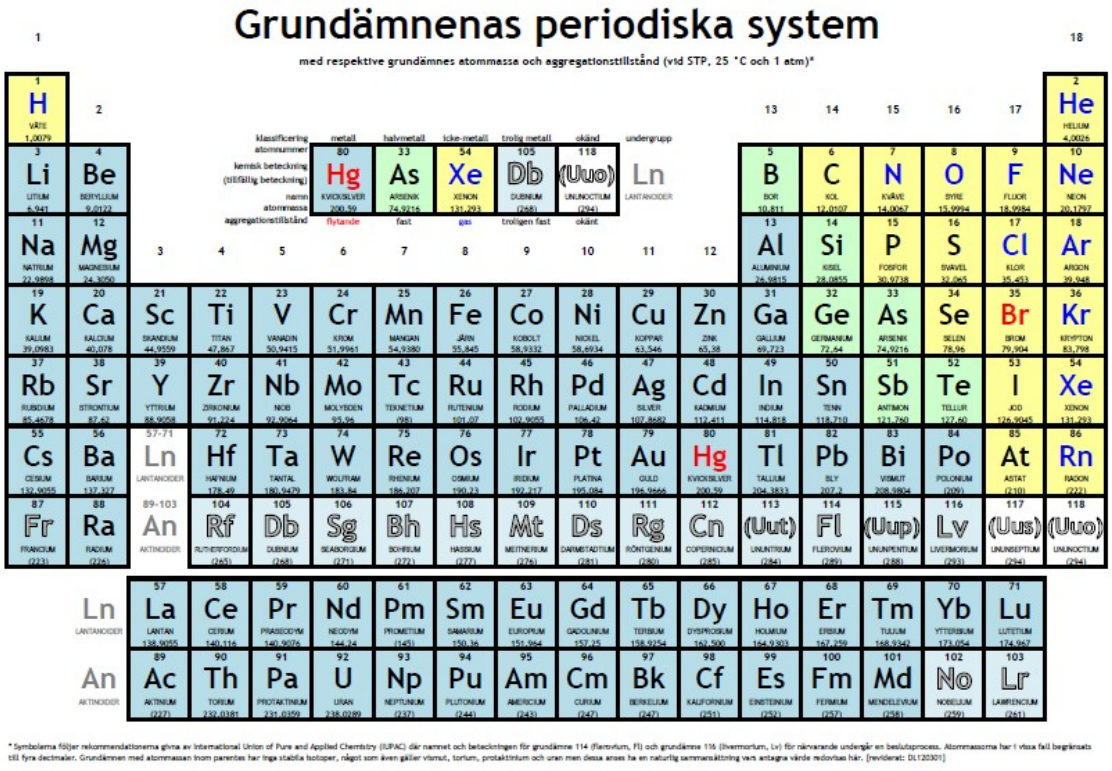
6 Appendix



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